# Organic Materials in Silico

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# Summary

Organic electronics have a wide range of applications, from utilizing the solar energy for electricity generation to devices that seamlessly integrate with biological surfaces. The virtually unlimited chemical space of organic molecules, while offering the possibility of ideal molecules for each of these applications, also makes it more challenging to find them. A common approach to navigating through this vast chemical space towards better performing devices is identifying design rules by correlating changes in molecular or morphological structure to the improvement of specific properties. Functionalizing organic molecules with polar side chains is one such design rule that has become a ubiquitous strategy in the search for the next generation organic materials. Such functionalization is often done with the aim of increasing the dielectric constant, which in turn is expected to weaken the interactions between the charge carriers and reduce their recombination. The performance of these molecules, however, varies drastically between seemingly similar molecules and between different applications.

This thesis elucidates, by advancing and applying computational methods, what happens at the molecular level by the inclusion of polar side chains and provides a deeper understanding of the interplay between molecular structure and dielectric and electronic properties, with the aim of guiding the field towards engineering better performing devices. A strong emphasis is given to both the accurate computation of the frequency-dependent dielectric constant and the understanding of the relevant dielectric contributions for organic electronics. The thesis also demonstrates how theoretical and spectroscopic methods can be used synergistically in order to obtain high resolution structural information of organic films with the aim of improving their thermoelectric and electronic properties. Additionally, the multiscale approach introduced in this thesis, which is readily applicable in various materials science and biophysics studies, allows approaching quantum mechanical accuracy using computationally much more feasible molecular dynamics simulations.

While increasing the dielectric constant of organic photovoltaic devices has been suggested as a pathway to improve their power conversion efficiency, it is often unclear whether the electronic or static dielectric constant will have this effect. In **chapter 2**, the effect of functionalizing molecules with polar side chains, often done with the aim of maximizing the *static* dielectric constant, on the *electronic* dielectric constant is investi-

gated. After establishing the reliability of the employed methodology, which is based on periodic coupled perturbed Kohn-Sham calculations, the electronic dielectric constant of various fullerene-based organic semiconductors was computed. The results unveil the undesirable correlation that the electronic dielectric constant decreases as the side chain increases in size. An important implication of these results is that one must study carefully which dielectric constant is the relevant one for the application of interest, as maximizing one dielectric contribution sacrifices the other. Computation of the time-dependent dielectric constant and investigation of the relevant time scales for organic electronics applications is done in chapters 4 and 5 by using molecular dynamics simulations, after the development of the necessary methodology in chapter 3.

The accuracy of force fields, which specify all intra- and intermolecular interactions of a system, determines the quality of molecular dynamics simulations. The common approach of having transferable, *atom-types*-based force field parameters sacrifices accuracy in favor of generality. In **chapter 3**, we present an alternative method named Q-Force, which derives these parameters from quantum mechanical calculations in an automated manner. First, it is demonstrated for a set of small molecules that a near quantum mechanical accuracy of the potential energy surface is achieved with these force fields without extra computational cost after the initial parametrization. Then, two studies on state-of-the-art molecules in the field of organic photovoltaics are presented, where the use of Q-Force is shown to improve the potential energy surface drastically in one case, and the HOMO/LUMO energy level distributions in blends of donor-acceptor molecules in another. This methodology is used in the following chapters in order to generate accurate force fields to study the dielectric and structural properties of organic materials.

The use of polar ethylene glycol side chains has become the preeminent strategy to increase the static dielectric constant of organic materials. Importantly, the increased dielectric constant is due to nuclear relaxations whose time scales would therefore determine the relevance of this increase for different organic electronics applications. In **chapter 4**, the time- and frequency-dependent dielectric constant of a representative fullerene derivative with ethylene glycol side chains is predicted using a computational protocol based on polarizable molecular dynamics simulations and a force field generated with the Q-Force methodology. Having the atomic resolution, we are able to pinpoint the different dielectric contributions to different fragments of the molecule and identify the molecular response that is causing the unusually high dielectric constant. Additionally, the extracted dielectric relaxation time suggests that ethylene glycol side chains may respond too slowly to provide Coulombic screening in organic photovoltaics but are likely fast enough in the case of organic thermoelectrics with much lower charge carrier velocities.

Following the establishment of the protocol for the computation of the time- and frequency-dependent dielectric constant in chapter 4, the highly different dielectric constants of seemingly similar molecules are studied in **chapter 5** in order to gain insight on how the dielectric response can be further enhanced and accelerated. A carefully selected series of fullerene derivatives with ethylene glycol side chains allowed studying the dielectric response in terms of both the number and length of the ethylene glycol chains, and also the choice of the group connecting the fullerene to the ethylene glycol chain. Such a selection, together with the computational protocol that allowed the separation of different factors contributing to the overall dielectric constant has enabled us to make several molecular design guides for future organic materials in order to enhance their dielectric constant further. The results also reveal that the experimentally observed rise of the dielectric constant within the kilo/megahertz regime for some molecules is likely due to the highly stretched dielectric response of ethylene glycols: The initial sharp increase over the first few nanoseconds is followed by a smaller but persistent increase in the range of microseconds.

Functionalizing molecules with ethylene glycol side chains has also been applied to improve the electronic properties of organic materials. As these properties are closely tied to both molecular and morphological structure, determining these structures is highly insightful, but on the other hand it remains challenging to do so experimentally in polycrystalline films. In **chapter 6**, two case studies are presented where the molecular packing in such films is resolved through a synergistic use of spectroscopic and theoretical methods for fullerene derivatives with ethylene glycol side chains. The results highlight the strength of such an approach that combines theory and experiments in order to gain insight into the intimate relationship between molecular structure, morphology, and electronic properties. More specifically, highly ordered and alternating layers of fullerenes and ethylene glycols are identified in both case studies, which are linked to the record n-type thermoelectric performance in the first case study and to the improvement of the transport properties with increasing ethylene glycol layer size in the second case study.

In short, three main topics covered in this thesis are the computation of the dielectric properties of organic semiconductors (chapters 2, 4, and 5), the methodology for quantum mechanically augmented force fields (chapter 3), and resolving crystal structures by a combination of theoretical and spectroscopic approaches (chapter 6). Potential future developments in these three fields are discussed briefly in **chapter 7** as an outlook. Overall, the findings of this thesis contribute to the goal of materials design based on computational approaches by improving existing models as well as the understanding of several property-structure relationships.

# Samenvatting

Organische elektronica heeft een breed scala aan toepassingen, van het gebruik van zonne-energie voor elektriciteitsopwekking tot apparaten die naadloos integreren met biologische oppervlakken. De vrijwel onbeperkte chemische ruimte van organische moleculen, die weliswaar de mogelijkheid biedt om voor elk van deze toepassingen ideale moleculen te maken, maakt het ook uitdagender om ze daadwerkelijk te vinden. Een gebruikelijke aanpak om door deze enorme chemische ruimte naar beter presterende materialen te zoeken, is het opstellen van ontwerpregels door veranderingen in moleculaire of morfologische structuur te correleren met de verbetering van specifieke eigenschappen. Het functionaliseren van organische moleculen met polaire zijketens is zo'n ontwerpregel die een alomtegenwoordige strategie is geworden in de zoektocht naar een volgende generatie van organische materialen. Zo'n functionalisering heeft ten doel de diëlektrische constante te verhogen, wat op zijn beurt naar verwachting de interacties tussen de ladingsdragers zal verzwakken en hun recombinatiekans zal verminderen. De prestaties van deze moleculen variëren echter drastisch tussen schijnbaar vergelijkbare moleculen en tussen verschillende toepassingen.

Dit proefschrift verduidelijkt door middel van ontwikkeling en toepassing van multischaal computationele benaderingen, wat er op moleculair nivo gebeurt als polaire zijketens opgenomen worden. Het werk geeft ook een dieper begrip van het samenspel tussen moleculaire structuur en diëlektrische en elektronische eigenschappen, met als doel het veld te leiden naar het ontwerpen van beter presterende materialen. Sterke nadruk wordt gelegd op zowel de nauwkeurige berekening van de frequentieafhankelijke diëlektrische constante als het begrip van de relevante diëlektrische bijdragen voor organische elektronica. Het proefschrift laat ook zien hoe theoretische en spectroscopische methoden synergetisch kunnen worden gebruikt om structurele informatie met hoge resolutie van organische films te verkrijgen zodat vervolgens hun thermo-elektrische en elektronische eigenschappen verbeterd kunnen worden. Bovendien maakt de in dit proefschrift geïntroduceerde multischaalbenadering, die direct toepasbaar is in verschillende materiaalkunde en biofysische studies, het mogelijk om kwantummechanische nauwkeurigheid te benaderen met behulp van computationeel veel meer haalbare moleculaire dynamica simulaties.

Hoewel het verhogen van de diëlektrische constante van organische fotovoltaïsche

materialen is voorgesteld als een manier om hun energieconversie-efficiëntie te verbeteren, is het vaak onduidelijk of de elektronische of statische diëlektrische constante dit effect zal hebben. In **hoofdstuk 2** wordt het effect onderzocht van het functionaliseren van moleculen met polaire zijketens, vaak gedaan om de *statische* diëlektrische constante te maximaliseren, op de *elektronische* diëlektrische constante. Na het vaststellen van de betrouwbaarheid van de toegepaste methodologie, die is gebaseerd op storingsrekening en die bekend staat als "periodic coupled perturbed Kohn-Sham", werd de elektronische diëlektrische constante van verschillende op fullereen gebaseerde organische halfgeleiders berekend. De resultaten onthullen een ongewenste correlatie: de elektronische diëlektrische constante wordt kleiner naarmate de zijketen groter wordt. Een belangrijke implicatie van deze resultaten is dat men zorgvuldig moet bestuderen welke diëlektrische constante de relevante is voor de betreffende toepassing, aangezien het maximaliseren van de ene diëlektrische bijdrage ten koste gaat van de andere. Het berekenen van de tijdsafhankelijke diëlektrische constante en onderzoek naar de relevante tijdschalen voor organische elektronicatoepassingen wordt gedaan in de hoofdstukken 4 en 5 met behulp van moleculaire dynamica simulaties, na de ontwikkeling van de benodigde methodologie in hoofdstuk 3.

De nauwkeurigheid van krachtvelden die alle intra- en intermoleculaire interacties van een systeem bepalen, is ook bepalend voor de kwaliteit van moleculaire dynamica simulaties. De algemeen gebruikte aanpak met overdraagbare, op atoomtypes gebaseerde, krachtveldparameters doet afbreuk aan nauwkeurigheid ten gunste van algemeenheid. In **hoofdstuk 3** presenteren we een alternatieve methode genaamd Q-Force, die de krachtveldparameters op een geautomatiseerde manier afleidt uit kwantummechanische berekeningen. Eerst wordt voor een set van kleine moleculen aangetoond dat een bijna kwantummechanische nauwkeurigheid van het potentiële energieoppervlak wordt bereikt met deze krachtvelden zonder extra rekenkosten na de initiële parametrisering. Vervolgens worden twee studies over "state-of-the-art" moleculen op het gebied van organische fotovoltaïsche cellen gepresenteerd, waarbij wordt aangetoond dat het gebruik van Q-Force het potentiële energieoppervlak drastisch verbetert in één geval, en de HOMO/LUMO-energienivo-distributies in mengsels van donor-acceptormoleculen in een ander. Deze methodologie wordt in de volgende hoofdstukken gebruikt om nauwkeurige krachtvelden te genereren om de diëlektrische en structurele eigenschappen van organische materialen te bestuderen.

Het gebruik van polaire zijketens van ethyleenglycol is de meest vooraanstaande strategie geworden om de statische diëlektrische constante van organische materialen te verhogen. Belangrijk is dat de verhoogde diëlektrische constante het gevolg is van kernbewegingen; daarom zouden de tijdsschalen daarvan de relevantie van deze verhoging voor verschillende organische elektronicatoepassingen bepalen. In **hoofdstuk 4** wordt de tijd-

en frequentie-afhankelijke diëlektrische constante van een representatief fullereenderivaat met ethyleenglycol zijketens voorspeld met behulp van een rekenprotocol gebaseerd op polariseerbare moleculaire dynamica simulaties en een krachtveld gegenereerd met de Q-Force methodologie. Met de atomaire resolutie zijn we in staat om de verschillende diëlektrische bijdragen van verschillende fragmenten van het molecuul te bepalen en de moleculaire respons te identificeren die de ongewoon hoge diëlektrische constante veroorzaakt. Bovendien suggereert de geëxtraheerde diëlektrische relaxatietijd dat ethyleenglycolzijketens mogelijk te traag reageren om Coulomb afscherming in organische fotovoltaïsche cellen op te leveren, maar dat ze waarschijnlijk snel genoeg zijn in het geval van organische thermo-elektrische systemen met veel lagere ladingsdragersnelheden.

Na het opstellen van het protocol voor de berekening van de tijd- en frequentie-afhankelijke diëlektrische constante in hoofdstuk 4, worden de sterk verschillende diëlektrische constanten van schijnbaar vergelijkbare moleculen bestudeerd in **hoofdstuk 5**, om inzicht te krijgen in hoe de diëlektrische respons verder kan worden verbeterd en versneld. Een zorgvuldige selectie van een reeks fullereenderivaten met ethyleenglycolzijketens maakte het mogelijk de diëlektrische respons te bestuderen in termen van zowel het aantal als de lengte van de ethyleenglycolketens, en ook van de keuze van de groep die het fullereen met de ethyleenglycolketen verbindt. Een dergelijke selectie, samen met het rekenprotocol dat de scheiding mogelijk maakt van verschillende factoren die bijdragen aan de algehele diëlektrische constante, heeft ons in staat gesteld verschillende moleculaire leidraden te geven voor toekomstige organische materialen met verbeterde diëlektrische constante. De resultaten laten ook zien dat de experimenteel waargenomen stijging van de diëlektrische constante binnen het kilo/megahertz-regime voor sommige moleculen waarschijnlijk het gevolg is van de sterk verlengde diëlektrische respons van ethyleenglycolen: de aanvankelijke sterke toename gedurende de eerste paar nanoseconden wordt gevolgd door een kleinere maar aanhoudende toename in de volgende microseconden.

Gefunctionaliseerde moleculen met zijketens van ethyleenglycol zijn ook toegepast om de elektronische eigenschappen van organische materialen te verbeteren. Aangezien deze eigenschappen nauw verbonden zijn met zowel de moleculaire als de morfologische structuur, kan het bepalen van deze structuren veel inzicht opleveren, maar aan de andere kant blijft het een uitdaging om dit experimenteel te doen in polykristallijne films. In **hoofdstuk 6** worden twee casestudies gepresenteerd waarin de pakking van moleculen in dergelijke films wordt ontrafeld door een synergetisch gebruik van spectroscopische en theoretische methoden voor fullereenderivaten met ethyleenglycol zijketens. De resultaten onderstrepen de kracht van een dergelijke aanpak die theorie en experimenten combineert om inzicht te krijgen in de nauwe relatie tussen moleculaire structuur, morfologie en elektronische eigenschappen. Meer specifiek: in beide casestudies worden

sterk geordende en afwisselende lagen van fullerenen en ethyleenglycolen geïdentificeerd. Deze houden verband met de record n-type thermo-elektrische prestaties in de eerste casestudy en met de verbetering van de transporteigenschappen met toenemende ethyleenglycollaag-grootte in de tweede casestudy.

In het kort, drie hoofdonderwerpen die in dit proefschrift aan bod komen, zijn de berekening van de diëlektrische eigenschappen van organische halfgeleiders (hoofdstukken 2, 4 en 5), de methodologie voor kwantummechanisch versterkte krachtvelden (hoofdstuk 3), en het oplossen van kristalstructuren door een combinatie van theoretische en spectroscopische benaderingen (hoofdstuk 6). **Hoofdstuk 7** geeft een vooruitblik op mogelijke toekomstige ontwikkelingen op deze drie terreinen. Over het geheel genomen dragen de bevindingen van dit proefschrift bij aan het doel om materialen te ontwerpen op basis van computationele benaderingen, door het verbeteren van bestaande rekenmodellen en het begrijpen van verschillende eigenschap-structuur relaties.

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| 2009-2014 | Koç University Vehbi Koç Scholar for exceptional academic performance (4 times) |
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## Publications

1. S. Sami, E. Yildirim, M. Yurtsever, E. Yurtsever, E. Yilgor, I. Yilgor, G. L. Wilkes, *Understanding the influence of hydrogen bonding and diisocyanate symmetry on the morphology and properties of segmented polyurethanes and polyureas: Computational and experimental study*, Polymer **2014**, 55, 4563.

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